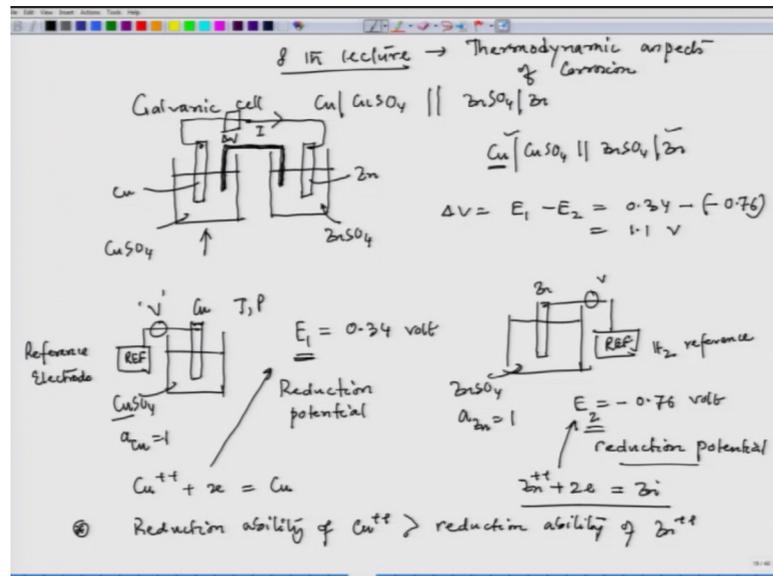**Corrosion - Part I**
Prof. Kallol Mondal
Department of Materials Science Engineering
Indian Institute of Technology, Kanpur

Lecture – 08
Thermodynamic aspects of corrosion-I

Let us start 8th lecture.

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On Corrosion and today we will talk about the thermodynamics will now start getting into the thermodynamics aspects of, Thermodynamics aspects of corrosion. Now let us look at a cell ok one of the very popular cells is galvanic cell of copper sulphate and zinc.

Now, the cell structure is like this if we have 2 container and in this container we have copper sulphate solution in this container we have zinc sulphate solution. And there we dip a copper plate and here we dip a zinc plate. So, this is zinc this is copper now in order to make it a complete cell. So, we have to have a salt bridge this is the salt bridge.

The salt bridge what it does, it connects 2 cells. So, that the charge transfer is possible between this 2 electrolytes this copper sulphates and zinc sulphates. Both are electrolytes it allows charge transfer. Now the external circuit we can connect it by a wire and once we connect it we will see that current is flowing. And this current flow would be in this direction so, this is the current flow direction.

And once we have this complete cell. So, that time the cell notation becomes like this. So, the complete cell notation would be copper, zinc. So, these 2 are electrodes so, this is basically one electrodes this another electrode. Now for the time being let us discontinue this external circuit this discontinue this external circuit. And now let us look at what is going on in the individual bicker. And in this bicker if we carefully notice and this bicker if we, for example, let us say this is the bicker where we have copper sulphate and copper rod this is copper sulphate and this is at a particular temperature pressure.

Now after some time, if we try to connect it to reference electrode. So, this reference is nothing but the reference electrode. And this reference electrode will be able to measure voltage. Now if we use hydrogen reference electrode and that hydrogen reference electrode is maintained at one atmosphere pressure and 298 Kelvin temperature. Then that time that hydrogen electrode reference potential is considered to be 0.

And then this with reference to this, if I measure this potential it is shows something around some potential E 1 and if this copper sulphate copper is maintained activity of copper is 1, then this value would become 0.34 volt. Similarly, on the other side if we have zinc plate, this is zinc sulphate and if maintains activity of zinc is maintained as 1. Then after sometime if we try to connect it to a reference electrode again, and if that reference electrode is happen is hydrogen reference electrode.

Then this potential it will also show some potential and that potential would be minus 0.76 volt. Now question is this is E 2 question is these potential whether it is a reduction potential or oxidation potential. For this course (Refer Time: 06:27) wherever we will talk about some potential unless, it is not mentioned clearly we will always talk about reduction potential.

So, this is nothing but reduction potential this is also reduction potential. Now these reduction potential means we are measuring that potential consideration considering the factor the reduction reaction is taking place. So, in this case the reduction reaction would be, this is the reduction reaction and in this case. So, from this it is very clear since it is potential reduction potential of this reaction is higher than the reduction potential of this reaction. So, the reduction ability of this copper plus plus iron is more than the reduction ability of zinc plus plus iron.

So, the statement what I am saying is reduction ability of copper plus plus is more than reduction ability of zinc plus plus. Once we have this situation then if we again complete the circuit, it will show initially if we try to see the potential difference between these 2. These potential difference would come as E 1 minus E 2 equal to 0.34 minus minus 0.76 equal to 1.1 volt.

So, this is the voltage what the system would experience before any current flow. Once we start this current flow; that means, once we short this entire circuit the reaction that would take place on the copper terminal and the zinc terminal would be decided by this, and this potentials; reduction potentials.

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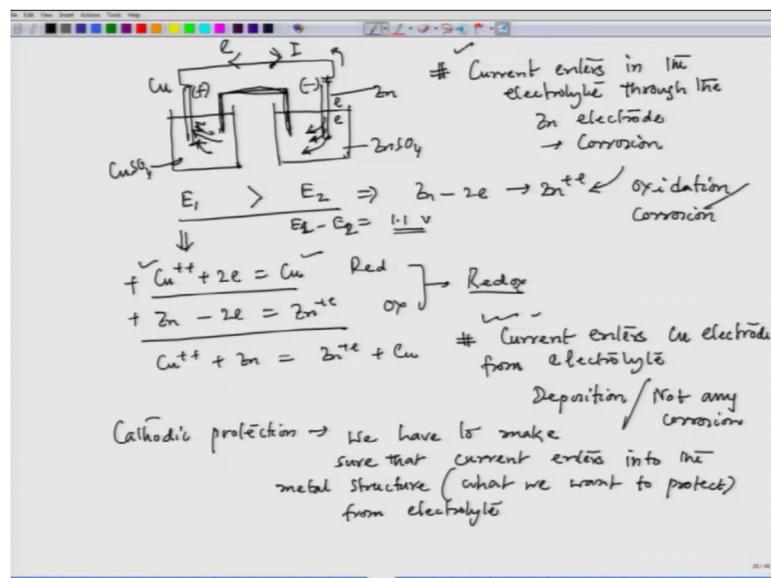
Now, let us see what is going on there cell. This is my salt bridge this is zinc plate, this is zinc sulphate, this is copper sulphate, this is copper plate. So now, we have connected them reactions are taking place. And we have seen that reduction potential of this terminal is greater than reduction potential of this terminal and since current is flowing. So, this terminal becomes positive terminal and this terminal becomes negative terminal.

Since we know that the electron flows current flows from positive to negative electrode. So, these are the sign of that 2 electrode, now what are the electrode reactions that are taking place and on this side since copper plus plus has got higher reduction ability. So, this reduction reaction would take place and in this case since zinc has got zinc plus plus

has got a lower reduction tendency. Now we have electron acceptance reaction; that means, in this case electron is consumed for this reaction.

So now the reduction reaction would not take place on the other electrode because, for this electron we have to have electron generation. And since the reduction ability of zinc plus plus is less than copper plus plus or other way around oxidation tendency of zinc plus plus zinc is higher than oxidation tendency of copper. So, the electron generation would start on the other electron, where zinc would release 2 electron and it form zinc plus plus iron.

So, the zinc would dissolve in this electrode and copper would deposit on this electrode. So now, interestingly now let us see what is happening so, we let us this is reduction and this is oxidation. So, if you add them we get this is the complete cell reaction and again if we remove this part and if we remove this part again it is becoming redox.

So, this redox reaction again is taking place, and in that way we have a definite current flow and that current flow would be utilized for glowing a light. Now interestingly as we see that the current flow is in this direction that is what we could fix the terminal the sign of the terminal, now here electron is flowing opposite to the current flow and that is what it should be.

So, the electrons are generated on this electrode and these electrons are flowing through this and then it is coming towards the copper electrode and those 2 electrons will be consumed by this reduction process. So now, question is how the current flows through the electrolyte. So now, current enters into the electrolyte through the zinc surface. So, current enters in the electrolyte, through the zinc electrode.

Now, when current enters into the through the zinc electrode to the electrolyte that time, what process is going on this process is going on. And this is what oxidation or corrosion. So, wherever corrosion is taking place remember, that current in that particular circuit enters through that metal rod or metal electrode into the electrolyte. So; that means, whenever current enters into the electrolyte through the metal we have corrosion.

Now, through the charge transfer this particular salt bridge will allow charge transfer. So, the through that particular salt bridge the charge is would go and the current would enter into the copper electrode from. So, this is one and second part is current enters copper

electrode, from electrolyte. So, what is going on the other side cathodic reaction or reduction reaction. And wherever current enters into the electrodes from the electrolyte we do not get corrosion rather we are getting deposition.

And not any corrosion; this two concepts are the backbone of the concept of cathodic protection. So, in the cathodic protection actually we have to divide something. So that the rod or the metal structure what we want to protect, the current should enter in to that particular structure from the electrolyte to that system.

So, that is the sole criteria; the sole criteria is this one for cathodic protection. So the cathodic protection; which is a basically a protection method from corrosion of any metal objects so, the primary concerted is we have to make sure that current enters into the metal structure, what we want to protect from electrolyte. And remember wherever any system anything wherever the corrosion is taking place since it has a electrochemical behavior electrochemical nature and there should be a current flow and you would see that wherever the corrosion is taking place there the current is actually entering into the electrolyte from the metal.

So, from this concept of corrosion it talks about corrosion how to know that where the corrosion is taking place and this is the concept of cathodic protection. So, 2 concepts we would know from this. Now we see that the potential difference E 2 minus E 1 sorry is basically E 1 minus E 2, we since we are taking about reduction potential is 1.1 volt before we sort the circuit.

Now this volt is useful for doing some electrical work. Now we can connect this electrical work with the free energy change and then that is the first step towards the consideration of thermodynamics in electro chemistry or for corrosion related aspects in our in our the kind of thing what we are discussing. Now let us see that part that how we can integrate free energy change with voltage difference.

Now, this free energy change since we are talking about a system, where we consider del G this is the free energy change Gibbs free energy change. When we do all the operations at one atmosphere so, the pressure we are maintaining fixed, and then we can consider Gibbs free energy. We can have another free energy term which is called work function which is a that will come when there is a constant volume process, but in case of constant pressure process we generally have this kind of we consider Gibbs or the G.

Now, before we talk about this relation, let us see independently what is going on in case of voltage difference and in case of free energy difference. Now there are 2 parts one is electrical energy. Let say in a circuit I supply q amount of charge and the voltage is del E then the amount of work electrical work would be q del E. And let us say the situation the system is working reversibly means it is maintaining dynamic equilibrium. And remember reversibility does not mean that it should come back to it is original position it has more to it and for the time being let us consider the reversible process is a very very slow process and every state is a very very small infinitesimal steps. So, that the dynamic equilibrium is maintained.

Now if we have some electrochemical reaction going on let us say m n plus ne this is the reduction reaction. And in this reduction reaction, for 1 mole of metal atom formation from metal ion we need any number of electrons will be needed to convert 1 M n plus to M. And we know 1 Faraday is basically the charge of 1 mole of electron.

So, how many charge we need to supply to get 1 mole of M would be equal to n F. So, this is the total charge, for 1 mole of M formation. So now, electrical work becomes is equal to n F del e. So, this is the total charge which is Q. Or you can put it as q. Now this F we can find out from charge of electron which is nothing but 1.60 10 to the power I think 0 2 or something. 10 to the power minus 19 coulomb and n 0 which is an Avogadro number is 6.023 and 6 10 to the power 23.

Now, then we have F equal to so, charge of one mole electron. So, F equal to n 0 into 1.602 into minus 19. We will see that it will come 9 6 4 8 3 something around that. So, this is written as 96500 coulomb so, this is the value of 1 faraday.

Now, let us look at the other side. So, this is the amount of electrical work that would be available to do for available from a galvanic cell, because in the galvanic cell we have chemical reactions which leads to potential difference, which will be useful for electrical work. Now on the other side if we consider G relation with h minus TS this is a famous relation and then we can write it as U minus PV minus TS

Now, if I consider change in G is equal to del U minus P del V minus V del P minus T del S minus S del T I can write this. Now since it is a constant pressure process pressure is constant this goes to 0; temperature is constant this goes to 0. So, temperature and pressure both are constant. So, we end up getting del U minus P del V minus T del S.

From the first law of thermodynamics we get del U equal to q minus W. Now in this case these W is the total work. Now let us say the system does mechanical work which is again some external pressure the volume expansion again some external pressure. So, it is basically the mechanical work and also if it does electrical work. So, it has a 2 contribution so, q minus W prime plus W mechanical.

And W mechanical with this particular system can be also written as P d V. So now, we have del G equal to q minus W prime this should be, sorry, we made great mistake here it should be positive, it should be positive. So, H is nothing but H equal to U plus P V. So, we made a mistake here. So, please correct it. So now, minus P del V plus P del V minus T del S. And what is W prime? W prime is electrical work.

Now again these 2 are cancelling in case of when we have both the work so, then it becomes del G equal to q minus W prime minus T del S. Now what is T del S term; let us

say the system is it is not specified whether the system is going reversibly or irreversibly. Now if the system goes on reversibly. So, then q reversible is nothing but T del S and now if the situation, then we can write equal to q minus W prime minus q reversible.

Now if we maintain that reversibility this q also is nothing but reversible q, reversible q. So, in a system these 2 are same if it is happening reversibly. So, then we get to if we go to the next slide.

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We see that delta G equal to nothing but W prime and on the other side, what we have received W prime which is electrical work is nothing but n F if we see this n F del E.

Here from the thermodynamics classical thermodynamics, we get del G equal to minus W prime and from electrical work concept we are get this. So, if we combine this we get delta G equal to minus n F del E. Now in the situation of copper zinc cell we generated del E equal to 1.1 volt. So, the total free energy change for the chemical reaction would be nothing but n F into 1.1 volt. So, this is the free energy change that is possible in the system and that free energy change is negative in nature. So, it leads to a formation it leads to do some electrical work

So, one of the major concept what we are getting is delta G equal to minus n F E this. And these del E is termed as E which is nothing but the difference. So, let us stop here will continue discussing this particular unique relation in our subsequent lectures.

Thank you.